

1

3,255,057

SENSITIZED AMMONIUM NITRATE EXPLOSIVES CONTAINING A HYDROGEN ION INDICATOR

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No Drawing. Filed Oct. 10, 1963, Ser. No. 315,378
3 Claims. (Cl. 149-2)

This application is a continuation-in-part of our copending application U.S. Serial No. 153,221, now abandoned.

This invention relates to novel low cost explosives and a method for their manufacture. More particularly, this invention relates to novel explosives containing a major quantity of ammonium nitrate in the form of prills and in addition nitromethane, a mixture of nitromethane with an alcohol, or an alcohol per se.

In the use of explosives, the need for safety is a problem which is ever present with workers in the field. Many explosives used in the field are compounded into a finished form at the factory and shipped from there to the point of use. During shipment, special precautions must be taken. Frequently, these precautions involve limitations on the routing of the explosives and the type of carrier, etc. Further, there are limitations as to the manner in which the explosives can be shipped and stored.

As a result of these requirements regarding shipping, storage, etc., dynamite explosives and other sensitive boosters are quite expensive to ship and store. This is reflected by a relatively high cost for the explosive material which must be borne by the ultimate user.

In many applications in the field, it is desirable to detonate an explosive in a small bore hole which is drilled in the rock or other material to be blasted. Since ammonium nitrate-fuel oil explosives require a large diameter bore hole (in excess of two inches in diameter), they are unsuitable for such operations. In these instances, dynamite must be employed.

In present blasting operations, it is frequently necessary to have on hand two types of explosives. The first type is an ammonium nitrate-fuel oil explosive which requires a relatively large diameter hole in which to detonate and which requires a booster charge of dynamite or other sensitive material for initiation of the explosion. The second type of explosive is dynamite which is relatively expensive and dangerous to work with. This explosive is used as a booster for ammonium nitrate-fuel oil explosives and is further used alone for blasting operations which require the use of small diameter bore holes. Thus, present blasting operations always require the presence of large quantities of a relatively sensitive explosive such as dynamite which must be transported and stored as an explosive. This creates constant safety hazards. Also, the use of two types of explosives creates storage and handling problems at the blasting site.

Many explosives are solids which are formed into a given shape in their manufacture. An illustration of this is the fact that dynamite generally comes in the form of sticks. By reason of their shape it is frequently difficult to get the desired quantity of explosive into the bore hole. In order to meet this problem, it is common practice in the field to slit the dynamite cartridges and tamp the explosive after it is inserted into the bore hole. This breaks down the sticks and forces the explosive into contact with the wall of the hole to get maximum packing density in the hole. Tamping is a time consuming and inherently dangerous operation since many explosives are somewhat shock sensitive.

In order to meet the above problems, it is an object of our invention to provide a low cost multipurpose ex-

2

plosive which is as cheap as ammonium nitrate-fuel oil explosives from a cost effectiveness standpoint (amount of rock removed per cost of explosive, drilling the bore holes, etc.) but which at the same time has properties which make it useful for applications now performed by dynamite. It is a further object of this invention to provide an explosive composed of ingredients which in themselves are not explosives so that they can be shipped and stored as ordinary articles of commerce. A still further object of this invention is to provide an explosive which does not require sensitive high explosive boosters, which will propagate readily in a small diameter bore hole, and which is free flowing so that it normally does not require tamping. Another object of this invention is to provide a method for compounding an explosive which method can be readily practiced in the field by inexperienced personnel without the use of elaborate mixing equipment. Additional objects will become apparent from the specification and claims which follow.

Our explosive composition comprises ammonium nitrate prills which are from about 25 to about 100 percent saturated (if 100 percent saturated, the prills are first evacuated in vacuo) with nitromethane, a mixture of nitromethane and a lower alcohol, or a lower alcohol. Depending upon the particular types of ammonium nitrate prills employed, the saturation point ranges from about 13 to about 18 percent by weight of the total explosive formulation.

In addition to explosives comprising prilled ammonium nitrate and nitromethane, our invention also includes explosives comprising prilled ammonium nitrate and a mixture of nitromethane with a lower alcohol. By lower alcohol we mean an alkanol such as ethanol, methanol, and propanol. Further, our explosives include prilled ammonium nitrate sensitized with a lower alcohol. The mixture of nitromethane and a lower alcohol with prilled ammonium nitrate is preferable to our explosives containing only a lower alcohol with prilled ammonium nitrate. It has been found that the lower alcohol-nitromethane mixture with prilled ammonium nitrate provides an explosive which has a higher brisance than prilled ammonium nitrate sensitized only with a lower alcohol. Further preferred explosive compositions comprise prilled ammonium nitrate sensitized with an alcohol-nitromethane mixture in which the alcohol comprises up to about 50 percent by volume of the sensitizer. A preferred alcohol for use in our explosive compositions, either alone or as the alcohol component in an alcohol-nitromethane mixture, is methanol since it is found that our explosives which contain this alcohol have superior brisance.

The ammonium nitrate prills used in our explosives are standard items of commerce and are used widely as fertilizer. By prilled we mean that the ammonium nitrate takes the form of spheroids as produced by dropping a super-saturated solution of ammonium nitrate through a shot tower through a countercurrent flow of dry air. The individual spheres of ammonium nitrate generally range in size from about 2000 to about 5000 microns in diameter. Although the particles are not completely uniform they are generally spherical in nature and are porous with respect to nitromethane, a lower alcohol, or a mixture thereof. As purchased, the ammonium nitrate prills are generally coated with an anticaking agent. The anticaking agent generally has little if any effect on the effectiveness of our explosives. Thus, our invention encompasses explosives in which either coated or uncoated prills of ammonium nitrate are used. Preferably, the ammonium nitrate prills are relatively uniform in size since we have found that such prills give a superior explosive. Nonuniform prills also give an explosive composition, however.

The explosive compositions of our invention have an oxygen balance ranging from about -25 to about +25.

Our explosives are readily mixed at the site by pouring the nitromethane, mixture of nitromethane with a lower alcohol, or a lower alcohol onto and through the prilled ammonium nitrate. Preferably, sufficient liquid sensitizer is added so as to substantially saturate the prills. One method by which this can be readily accomplished is by adding excess liquid and pouring off the excess after the prills have soaked for a period of a few minutes or longer. Since the quantity of liquid absorbed by the prills and the over-all oxygen balance of the explosive is determined by their porosity, it is not necessary for the worker to weigh the ingredients or perform any calculations in formulating the explosive. Rather, all he has to do is add the liquid sensitizer until the prills are saturated and then pour off the excess liquid. In one typical case, approximately one gallon of sensitizer per 50 pounds of ammonium nitrate prills gives an acceptable explosive.

Our preferred explosive compositions, therefore, are those in which the ammonium nitrate prills are saturated with sensitizer, since this composition makes its extremely easy for the worker to mix the ingredients in the field.

In order to obtain best results, our explosive compositions should not be allowed to stand for any prolonged period of time in contact with air. When this happens some of the liquid sensitizer can evaporate off to give a less effective explosive. In order to prevent this from happening, the explosive should be used within a few hours after mixing or else stored in a vapor-tight container so as to prevent evaporation of the liquid sensitizer.

Incorporated into our liquid sensitizer is a dye which colors the prills after the sensitizer is mixed with them. A particular dye which we employ is a hydrogen ion indicator or pH indicator such as diethylaminoazobenzene or Brilliant Oil Yellow #2625, as manufactured by National Aniline Corporation, which has a yellow color. Because of the color of the dye, the prills take on the color of the dye when they are saturated with the sensitizer. Sufficient dye is employed so that the dye is about .0065 percent by weight of the total explosive composition. This informs everyone dealing with the material that the explosive is ready for use and should be treated as an explosive. The dye changes color, from yellow to red, in the presence of acid of a pH of about 4.4. After the explosive has set for some time so that a portion of the sensitizer has evaporated, the yellow dye takes on a red color on the surface of the mixed explosive due to the ammonium nitrate. This indicates to people dealing with the explosive material that additional sensitizer is needed to bring the explosive back to full strength.

In order to further illustrate our invention, there are presented the following examples in which all parts and percentages are by weight unless otherwise indicated.

Example I

To 84 parts of prilled ammonium nitrate were added 16 parts of nitromethane. The explosive composition was then subjected to a number of tests as follows:

Columnar propagation and plate dent.—A 12-inch long spiral fabricated cardboard tube having an interior diameter of one inch and a wall thickness of one-eighth of an inch was filled with explosive. Following this, a No. 8 electric blasting cap was inserted in the top of the explosive column and the material was detonated. On detonation the entire column exploded and the tube was blown apart along its entire length.

When the above test was repeated using a two-inch inside diameter tube, the same results were obtained. In this test, the cardboard tube rested upon a one-inch thick aluminum plate which was backed up with four inches of steel. On detonation it was found that a dent was made in the plate having a maximum depth of 0.165 inch.

Bulk density.—A small sample of the explosive was placed in a graduated cylinder and weighed so as to determine its bulk density. The bulk density was found to be 0.927 gram per cc.

Underwater pressure test.—A one-pound sample of explosive was placed in a polyethylene bag having a cylindrical shape. The bag was about three inches in diameter and had a length of approximately five inches. After inserting the explosive in the bag, a Du Pont E-83 detonator containing 3.1 grains of Du Pont 50-25-25 ignition mix, 3 grains of lead azide, and 13.5 grains of pentaerythritol tetranitrate (PETN) was placed in the approximate center of the explosive charge and the charge was placed in a cylindrical tank having a diameter of 20 feet and filled with water. Approximately four inches from the wall of the tank was placed a transducer at a location which was approximately six feet below the water level and about four feet from the bottom of the tank. The charge was placed at the same depth as the transducer and approximately six feet from it along the major diameter of the tank. The transducer was connected to an oscilloscope which was calibrated to read the pressure produced in the tank. On explosion of the charge a peak underwater pressure of 16,700 pounds per square inch (p.s.i.) was recorded.

Impact sensitivity (Bureau of Mines).—A 20 milligram sample of explosive was tested by the standard Bureau of Mines impact sensitivity apparatus as generally defined in U.S. Bureau of Mines Bulletin 346 (1931). The test involved dropping a two kilogram weight a measured distance against a 20 milligram (mg.) sample of explosive. The results obtained are normally reported in terms of the minimum height in centimeters (cm.) at which the explosive detonated 100 percent of the time, the minimum height at which the explosive detonated 50 percent of the time, and the maximum height at which the explosive detonated 0 percent of the time. These results are meaningless in the present case since the sample failed to explode when the two kilogram weight was dropped from a height of 100 cm. onto the 20 mg. sample. This was the limit of calibration of the test apparatus. As a comparison it was found that RDX (a standard military explosive whose chemical name is cyclotrimethylene trinitramine) detonated 100 percent of the time at a minimum height of 30 cm., 50 percent of the time at a minimum height of 22 cm., and 0 percent of the time at a maximum height of 18 cm.

Heat sensitivity test.—A small sample of the explosive was placed in an aluminum cup which was placed on a bath of Wood's metal. The bath was slowly heated to determine the temperature at which the explosive would burn. Readings were taken at 20° F. intervals and the bath was maintained at a constant temperature for one minute at each of these intervals. When the bath reached a temperature of 700° F., the explosive burned after 6½ seconds.

Example II

To 84 parts of prilled ammonium nitrate were added 16 parts of a mixture comprising 30 volume percent of methanol and 70 volume percent nitromethane. The explosive was then subjected to several tests as described in Example I. It detonated completely in the two-inch columnar propagation test when initiated by a Du Pont E-83 cap and made a dent in the one-inch aluminum plate which had a maximum depth of 0.182 inch. The bulk density of the material was 0.891 gram per cc. and a one-pound sample gave a reading of 17,000 p.s.i. in the underwater explosion test. Impact sensitivity was in excess of 100 cm. for 100 percent and 50 percent explosion and was 95 cm. for 0 percent explosion.

Example III

To 84 parts of prilled ammonium nitrate were added 16 parts of a 50-50 volume mixture of nitromethane with methanol. The explosive was found to have a bulk den-

sity of 0.822 gram per cc. It detonated completely in the two-inch columnar propagation test and gave a plate dent having a maximum depth of 0.10 inch. Its impact sensitivity was in excess of 100 cm. for 100, 50, and 0 percent detonation.

Example IV

When Example IV was repeated employing isopropyl alcohol in place of methyl alcohol, the explosive composition obtained detonated completely in a steel pipe. Also, when the above examples are repeated using lower amounts of the liquid sensitizer, down to 25 percent saturation of the prills, good results are obtained.

A comparative test of our explosives with one which was superficially similar involved the preparation of an explosive containing 90.3 weight percent of prilled ammonium nitrate, 5.0 weight percent of nitromethane, and 4.7 weight percent of finely ground graphite powder. This material was thoroughly mixed so as to uniformly distribute the graphite powder and nitromethane within the explosive. It was then tested in the underwater explosion test, as described in Example I, using a one-pound sample. The explosive failed to fire with an E-83 blasting cap as used in the previous examples.

As set forth in the foregoing description, our explosives serve a dual function since they can be used in place of dynamite but yet at the same time are cheaper from a cost effectiveness standpoint than ammonium nitrate-fuel oil mixtures. Further, our explosives are readily formed in the field and are composed of ingredients that are not in themselves explosives. Thus, the ingredients forming our explosives can be shipped and stored as ordinary articles of commerce. This results in our explosives being both cheap and safe to ship and store.

In addition to being cheap and safe, our explosives are quite powerful. Thus, it has been observed in field testing that our explosives are more powerful than dynamite. This, coupled with their free flowing properties and ability to detonate in small diameter bore holes when completely unconfined, makes them admirably suitable for a number of applications in which dynamite is presently employed.

Our explosives cannot directly replace dynamite since some dynamites can be ignited under water or in wet bore

holes. In contrast, our explosives are rendered ineffective by coming in contact with water. This does not present a serious problem, however. When it is desired to use our explosives in applications where they come in contact with water, they can be placed in a water repellent container such as a polyethylene bag as employed in the underwater explosion test.

Having fully defined our explosive compositions and their mode of preparation, we desire to be limited only within the lawful scope of the appended claims.

We claim:

1. An explosive consisting essentially of ammonium nitrate prills and a liquid sensitizer selected from the group consisting of nitromethane, and a mixture of nitromethane and a lower alkanol, said explosive having an oxygen balance from about -25 to about +25, and a hydrogen ion indicator.

2. An explosive composition consisting essentially of ammonium nitrate prills which are from about 25 to about 100 percent saturated with nitromethane and about .0065 percent by weight diethylaminoazobenzene.

3. An explosive consisting essentially of ammonium nitrate prills and a liquid sensitizer selected from the group consisting of nitromethane, a mixture of nitromethane and a lower alkanol, and a lower alkanol, said explosive having an oxygen balance from about -25 to about +25 and containing a hydrogen ion indicator.

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